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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Silicon Carbide Articles and Methods of Forming them

(A Communication from The Carborundum Company, a Corporation organized and existing under the Laws of the State of Delaware, United States of America, of Niagara Falls, in the County of Niagara, and State of New York, United States of America).

I, Arthur Abbey, a British Subject, of 111/112, Hatton Garden, London, E.C.1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a novel refractory material and to the method of making it. The object of the invention is to produce a refractory composed of substantial amounts of self-bonded silicon carbide, which refractory can be made in relatively thin sections, which has a high load carrying capacity, which is highly resistant to thermal shocks, and which is highly oxidation resistant. The refractory material covered by the present invention may be used as setter tiles (i.e. thin flat slabs), bricks, and various other articles of any shape desired for use particularly in applications where a material having good strength at elevated temperatures is required.

The method of the present invention is distinguished from the prior art, in several important respects, one of which being that a relatively low firing temperature is required, and another of which is the absence of free carbon in the finished product. Because a low temperature is used, the process results in substantial savings because of the cost of power or fuel required to fire the refractory and also because a cheaper, lower temperature kiln may be used in its manufacture than heretofore. Bonded refractory materials containing a substantial amount of self-bonded silicon carbide, which are made by use of prior-art methods, have been found to have relatively poor mechanical strengths at elevated temperatures and to be prone to the development of cracks as a consequence of rapid changes of temperature. On the other hand the refractory of the present invention may be made in very thin sections where the particular application requires it, and yet will sustain high stresses throughout a long period of time at elevated temperatures. Such refractory will endure numerous rapid changes of temperature without cracking or sagging, and is also highly resistant to oxidation at high temperatures.

The method of the present invention consists, in one modification thereof, in heating an intimate mixture of finely divided carbon and finely divided silicon which have been moulded and formed to the desired shape, at a relatively low temperature, namely, from approximately 1200° C. to 1500° C. When approximately stoichiometric proportions are used and the mixture is so heated for a suitable length of time under reducing or non-oxidising conditions the carbon and silicon react substantially completely to form silicon carbide without the production of free carbon.

Thus, according to this invention, a refractory article comprises cubic silicon carbide crystals interlocked and at least partially inter-diffused with each other with the absence of free carbon, with or without a granulated refractory filler material.

Such silicon carbide is not the type obtained in the silicon carbide furnace which is conventionally used in the prior art, wherein a mixture of sand and carbon is packed around an elongated graphite core and is heated to an extremely high temperature, as for example, from 2000° C. to 2600° C. The product resulting from such conventional method of manufacture is in the form of either large platy crystals or elongated needle-like crystals of hexagonal silicon carbide. In the method of the present invention, because of the low tempera-

tures employed the product is composed wholly or in part in the form of very small crystals, so small in fact, that when examined by the naked eye, they appear to be amorphous, and which, upon examination, as by use of X-ray diffraction patterns, is found to be cubic silicon carbide.

The product may consist substantially wholly of such cubic silicon carbide with the minute crystals closely interlocked so that the product has a very high mechanical strength. In modifications of my invention, which are employed where products having properties different from those of the product above described are desired, there is employed a substantial amount of filler material which is incorporated initially with the mixture of carbon and silicon. Such filler material may be, for example, ordinary hexagonal silicon carbide of one or more mesh sizes, alumina, mulite, kyanite, or other refractory grain, or it may be a clay.

When sufficient clay is used to act as a supplementary bond, as for instance when 20—30% by weight of the product is employed, the product has a mechanical strength and toughness which allow it to withstand especially hard use in the way of mechanical and heat shocks.

Two or more of such filler materials may be used together. In cases where such filler materials are used, the product consists of such filler uniformly distributed throughout the resulting refractory shape and a bond of interlocked cubic silicon carbide crystals. It is possible, by use of the filler or varying amounts of clay to modify and predetermine such properties of the refractory as mechanical strength, coefficient of expansion, heat conductivity, and resistance to thermal shock.

The cubic silicon carbide, formed as a result of the reaction between the carbon and silicon of the mixture, bonds itself and the filler material, if such is used, into a strong coherent mass by reason of the interlocking of the cubic silicon carbide crystals with each other and the granular filler, and by reason of the at least partial interdiffusion between adjacent cubic silicon carbide crystals. When the refractory is employed at temperatures above that at which it was formed, it is self-strengthening, since such temperature will further the inter-diffusion between silicon carbide crystals. If such temperature is high enough, the cubic silicon carbide changes partially or wholly to hexagonal silicon carbide with the crystals strongly interlocked or joined. The product of the present invention is therefore self-strengthening under high temperature operating conditions.

The process of the present invention is carried out as follows: The components of the mixture of which the refractory is to be composed, as for instance, finely divided carbon and finely divided silicon, if no filler is to be employed, or such materials plus hexagonal silicon carbide in the desired grit size where such material is to be used as a filler, are thoroughly mixed for a long enough time to insure uniform distribution of the components throughout the mixture. In order to permit the mixture to be molded, a temporary binder is added. Any of the usual and well known temporary binders or resins of both dry and liquid form may be used alone or in workable combinations. The mix is then formed by the usual forming methods, under pressures equivalent to 1000—7000 lbs. per square inch, after which the shapes are slowly dried in an oven at moderate temperature. After drying, the shapes are fired in a kiln under either reducing or non-oxidising conditions. In one method the shapes are packed in coke which, upon heating, provides a reducing atmosphere. In another method, a furnace into which is introduced either a reducing or non-oxidising gaseous atmosphere is employed.

The heating cycle employed for such firing operation may obviously be varied considerably. Naturally, the cycle should be such as to heat the shapes gradually enough to prevent their being cracked. The shapes should then be held at a temperature of from 1200° to 1500° C., or slightly above, for a long enough period to insure complete reaction between the carbon and the silicon metal. No definite figures can be given for the length of holding of the product at this temperature since this obviously depends to some extent upon the thickness of the cross-section of the product. As an example only, where a relatively thin setter tile is made, it has been found satisfactory to heat the product from room temperature to approximately 1250° C. in a period of twelve hours, then to slowly raise the temperature over a period of eighteen hours to about 1450° C., and to cool it back to room temperature at a rate comparable to the rate of heating.

As has been indicated above, the composition of the product may be widely varied, depending upon the use for which it is intended. The ratio of the weight of silicon to the weight of carbon employed in the practice of this invention should be such generally to provide for their complete reaction to form silicon carbide thus avoiding the presence of free carbon

in the finished product. In other words, the ratio should be at least the stoichiometric ratio of silicon to carbon, namely, 2.34. In some instances it is desired that metallic silicon be present as such in the finished product; in these cases the silicon is employed in excess of the stoichiometric ratio. For the purpose of my invention the ratio $\frac{\text{weight of silicon}}{\text{weight of carbon}}$ should usually lie between approximately 2.34 and 3 depending upon the conditions employed in firing. Where an excess of silicon is employed the product has a shiny submetallic appearance and possesses more strength than where elemental silicon *per se* is not present.

It has been found that the resulting refractory is stronger and more oxidation resistant when an excess of silicon is employed than when it consists of cubic SiC alone. This may possibly be explained by the formation of coatings of silicon on the grain. Subsequent oxidation of the silicon provides a protective coating for the grain; such a formation of SiO_2 *in situ* effects an enhancement in strength of the refractory at high temperatures.

As indicated above no filler need be used in the mixture in the practice of the invention. In some instances, granular hexagonal silicon carbide uniformly distributed throughout the product has been found to be desirable. It has been found that a satisfactory product results when using such granular hexagonal silicon carbide as a filler, when amounts lying anywhere within the range from 0 to 80% by weight of the product are employed. When clay is used as a filler or supplementary bond, the amounts of clay may lie anywhere within the range from 0 to 30% by weight of the product. In no instance, whether one or more fillers are used, does their sum exceed 90% by weight of the product. The refractory of the present invention has a composition by weight falling within the following limits:

Refractory filler	0—90%
Supplementary clay bond	0—30%
Si (total)	6—75%
C	2—30%

the sum of the supplementary clay bond and refractory filler, if both are used together, not to exceed 90%, the ratio $\frac{Si}{C}$ lying between 2.34 and 3. In the finished refractory, uncombined silicon plus cubic silicon carbide compose from 20—100% by weight; and uncombined silicon from 0—16.65% by weight of the product.

For purposes of illustration only, and not in any way to be considered as restricting the invention, the following examples of typical mixtures falling within the scope of the invention are given: All parts given below are by weight; sufficient water is added in each instance to produce the working properties needed for the forming process to be employed. Likewise the amounts of temporary binders employed will be such as to suit the requirements of process to be used.

The numeral associated with the word "mesh" in certain of the following examples indicates the number of strands and spaces per linear inch of the screen through which the materials have been passed.

Example I

	Parts
Powdered Silicon	70
Carbon	30
Temporary Binder	0—5

Example II

	Parts
14 mesh and finer hexagonal silicon carbide	60
Powdered silicon	28
Lamp Black	12
Temporary binder	0—5

Example III

	Parts
14 mesh and finer hexagonal silicon carbide	75
Powdered silicon	20
Lamp Black	7½
Temporary binder	0—5

Example IV

	Parts
68 mesh and final hexagonal silicon carbide	30
Powdered silicon	28
Lamp Black	12
Clay	20
Temporary Binder	0—3

Use of a non-oxidizing or reducing atmosphere during the burning of the product of the invention has been found to be an important feature of the method. Such atmosphere prevents contamination of the product or change of weight thereof by reason of oxidation. Furthermore, by use of such atmosphere it can be told with a certainty what the composition of the burned product will be from a consideration of the character and amount of the components of the mixture from which it was made. Thus, if a stoichiometric ratio of carbon and silicon is employed in the mixture, one is assured that the product will consist substantially

wholly of cubic silicon carbide, with no appreciable excess of either carbon or silicon. Without the use of such atmospheres there occur relatively large losses of silicon by vaporization and losses of carbon by oxidation especially from the outer portions of the product; when this takes place the composition of the product is not uniform and is not subject to the rigid control made possible by the practice of my invention.

Although silicon has been described as being used in that form, it is obvious that the silicon may be derived from finely comminuted alloy which is employed in the mix instead of silicon. Such alloy may be, for example, an aluminium-silicon alloy or a ferro-silicon having a high silicon content, for example, 90%. In the examples given above the carbon is added to the mixture in the form of lamp black. It is to be understood that carbon in other finely divided forms may be employed in the process. Thus, for instance, powdered retort carbon or powdered coke may be employed in the practice of the invention.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, declare that what I claim is:—

1. A refractory article comprising cubic silicon carbide crystals interlocked and at least partially inter-diffused with each other with the absence of free carbon, with or without a granulated refractory filler material.

2. A refractory article according to claim 1, and comprising silicon carbide grain of hexagonal crystal habit interlocked with the cubic silicon carbide crystals, and distributed throughout the article in a substantially uniform manner.

3. A refractory article according to claim 2, wherein the silicon carbide grain of hexagonal crystal habit is present in up to 80% by weight of the article.

4. A refractory article according to any of the preceding claims, wherein there is also present elemental silicon.

5. A refractory article according to claim 4, wherein the silicon plus the cubic silicon carbide comprises from 20% to substantially 100% by weight of the article, the elemental silicon being present in amounts up to 16.66% by weight of the article.

6. The process of manufacturing refractory articles comprising forming a mix of substantial amounts of powdered silicon and finely divided carbon, the ratio of the weight of the silicon and the weight of finely divided carbon in the mix lying between 2.34 and 3, mixing the components thoroughly with a temporary binder so that the mixture is rendered workable, forming the mixture to shape, drying the shape and firing in a non-oxidizing or reducing atmosphere at a temperature of at least 1200° C. for such a period of time that a substantial portion of the silicon reacts with the finely divided carbon to form cubic silicon carbide crystals which are so interlocked with each other that a mechanically strong shape results.

7. A process of manufacturing refractory articles according to claim 6, wherein the firing of the formed mixture is carried out within a temperature range of 1200° C. to 1500° C.

8. A process of manufacturing refractory articles according to claim 6 or claim 7, wherein there is incorporated in the initial mix a refractory filler material.

9. A process of manufacturing refractory articles according to claim 8, wherein said refractory filler material comprises silicon carbide grain.

Dated this 4th day of July, 1947.

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